The application:
Standards for optical power measurements at NIST (and elsewhere)

The science:
Identification of tube size, spacing, species and dielectric function
- rapid, inexpensive, uncertain

Spectral Responsivity of pyroelectric detectors coated with carbon nanotubes

Optoelectronics Division

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Materials Reliability

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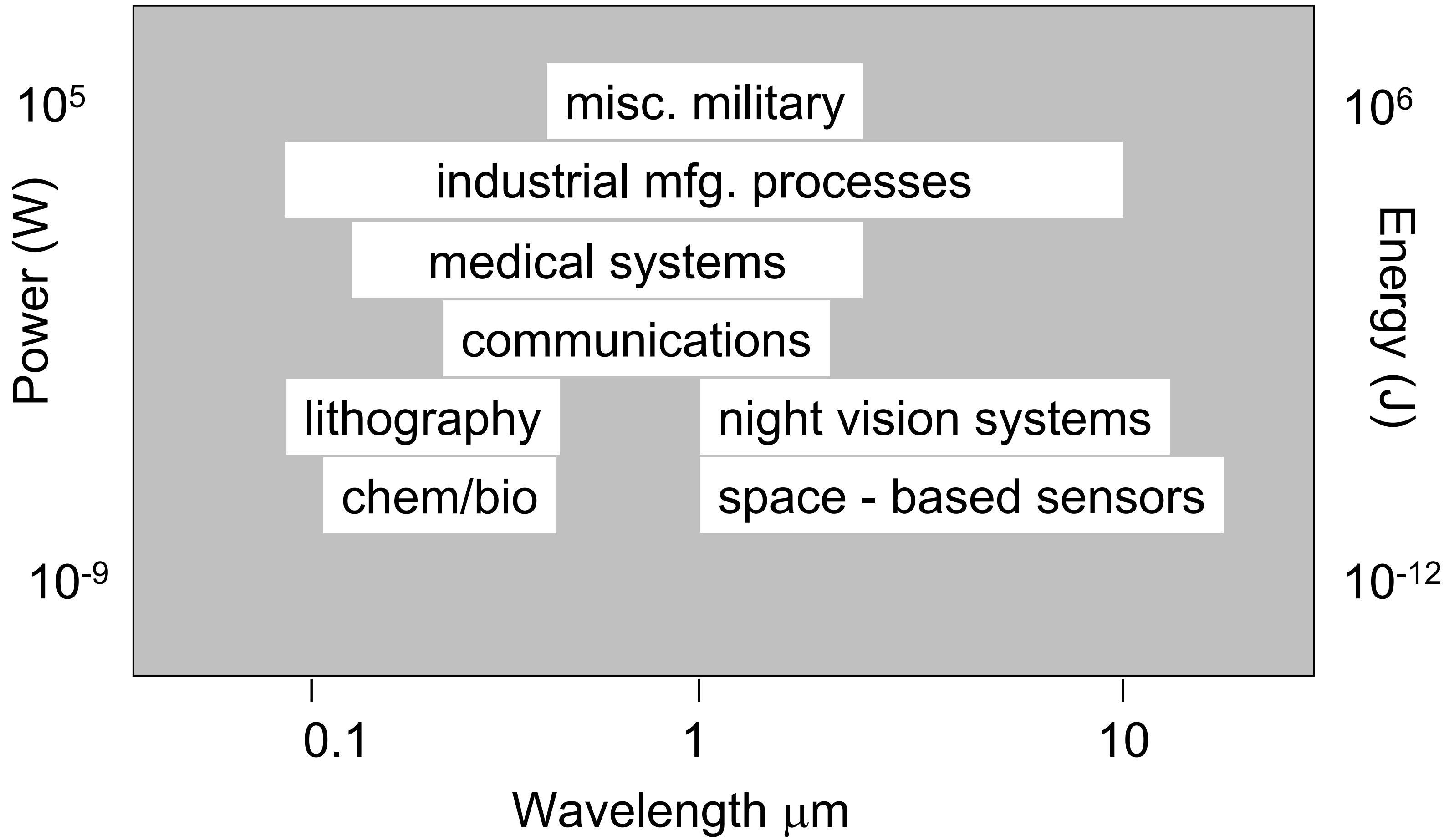
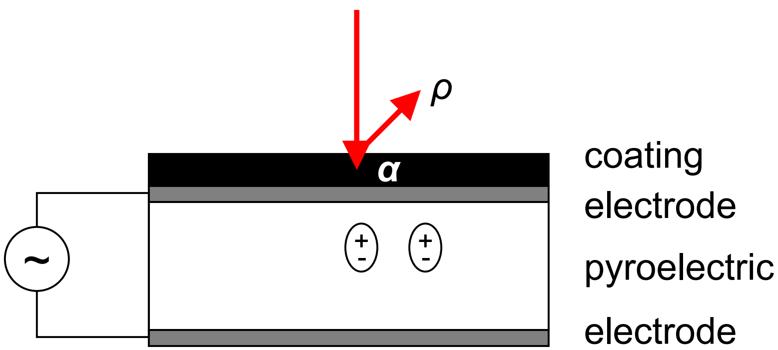
Motivation



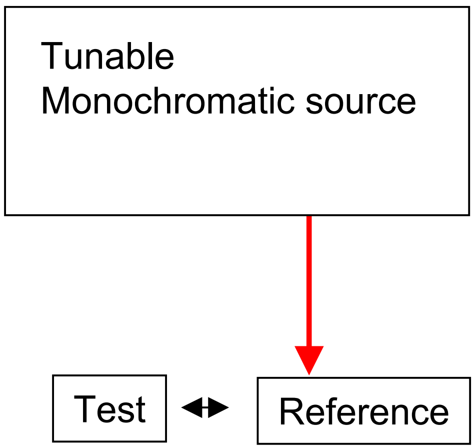
The next generation of detectors for laser power and energy measurements traceable to NIST

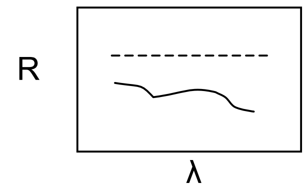
Detector operation and measurement



$$i = \alpha p \frac{A}{h} \int_0^h \frac{d\theta}{dt} dz$$

Responsivity measured by direct substitution
U ~ 0.25 % to 1.25 %

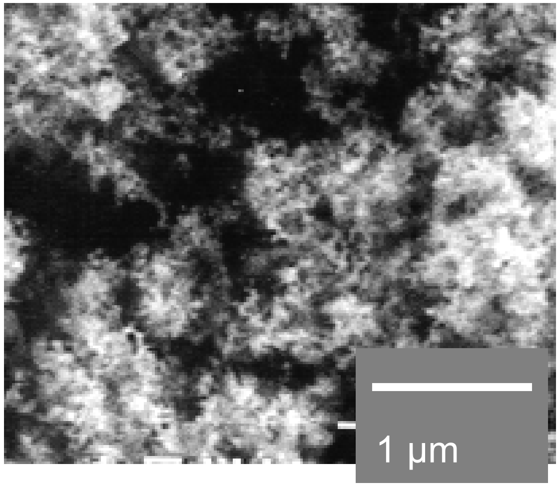




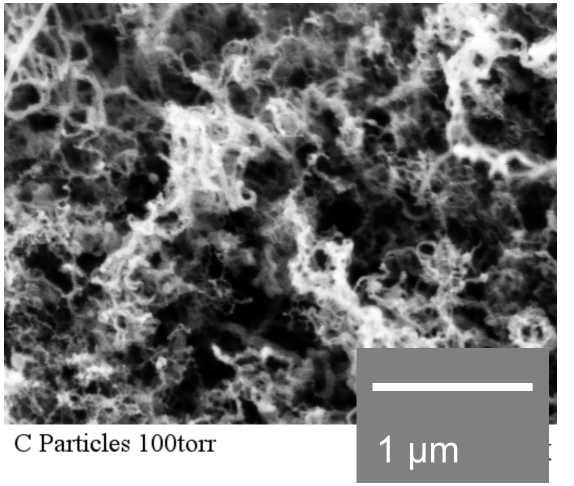
$$R = \frac{Test\,(Amps)}{Reference\,(Watts)}$$

*This application is for coatings for all **thermal** detectors, the responsivity of which depends on spectral properties of the coating*

Appearance



Au Black, 1 Torr



Carbon SWNTs, 100 Torr

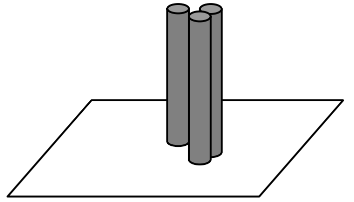
Began with the idea that carbon nanotubes look black (and that they have desirable thermal and mechanical properties)

learned of the complexities (or simplicities) of NT structure

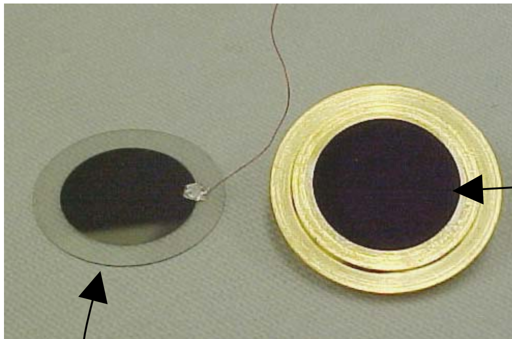
learned of the possibilities to optimize permittivity using effective medium theory (bulk SWNT and MWNT) by varying processing parameters

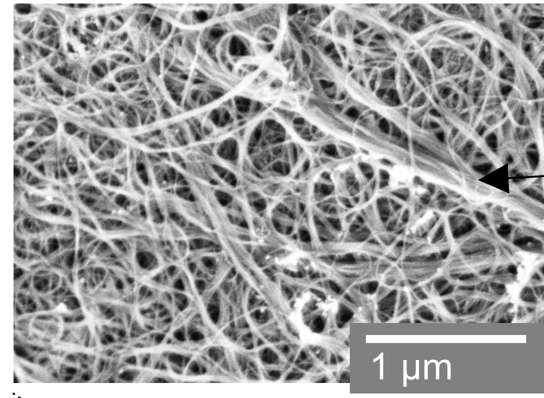
adding impurities controlling tube diameter, multiplicity, orientation, etc.

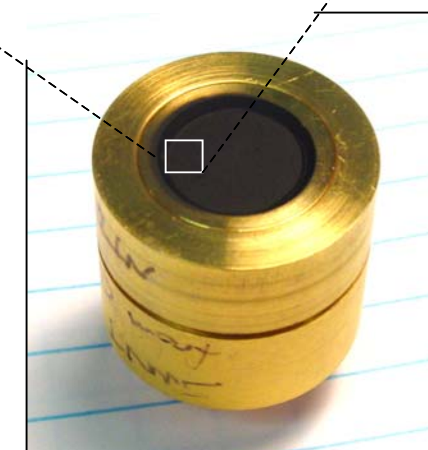
Detectors and Coatings
Measurements
Modeling
Cleaning



Bulk tubes on a pyroelectric detector





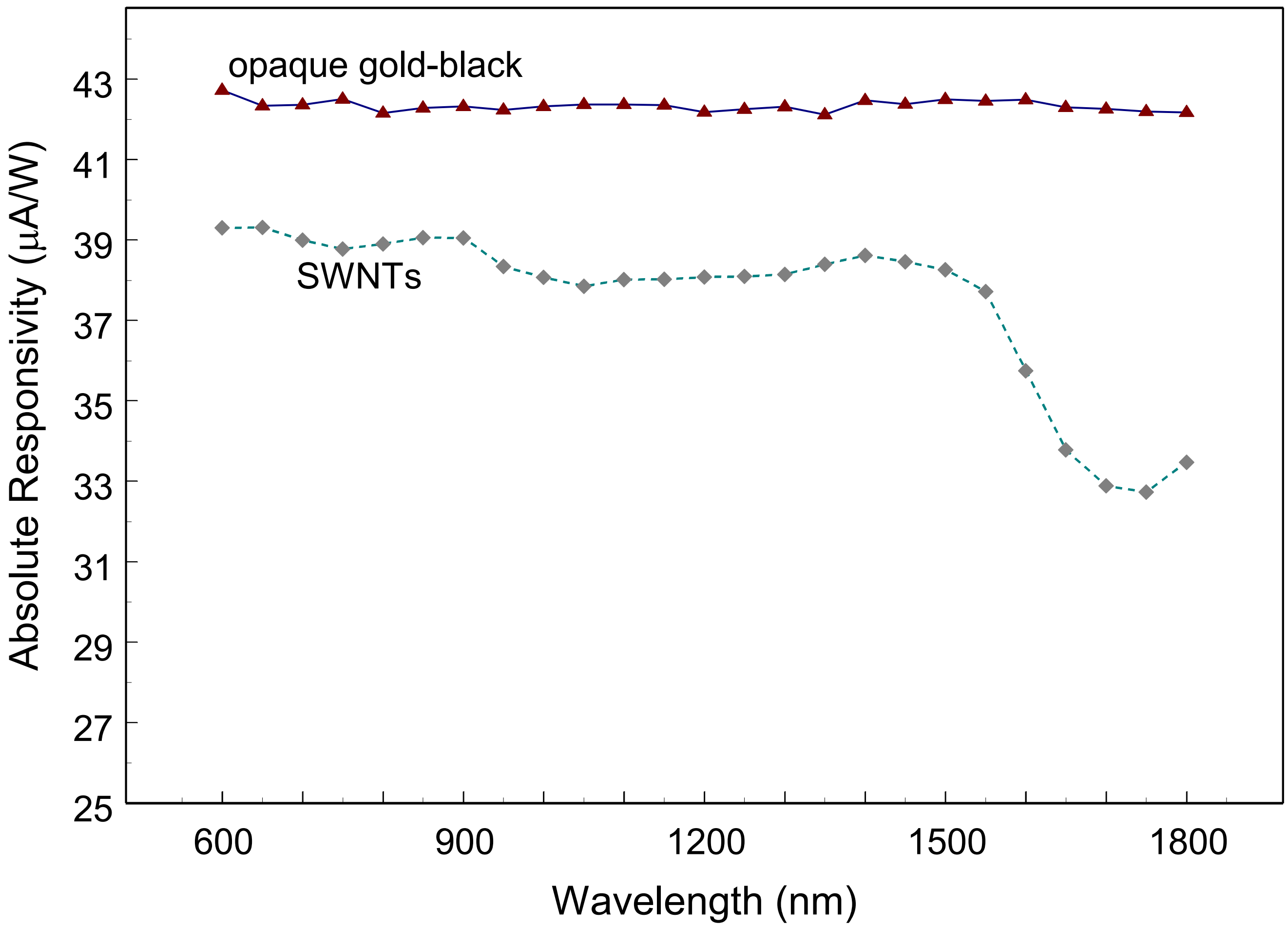


Coating preparation (2 detectors)

1. 2.6 torr Au-black (~ 20 µm thick)

2. A 2 mL aliquot of a chloroform (CHCl3) suspension of SWNTs (~ 20 µm thick)

Measured detector response



total uncertainty 1.25 %

Effective medium approximation (EMA)

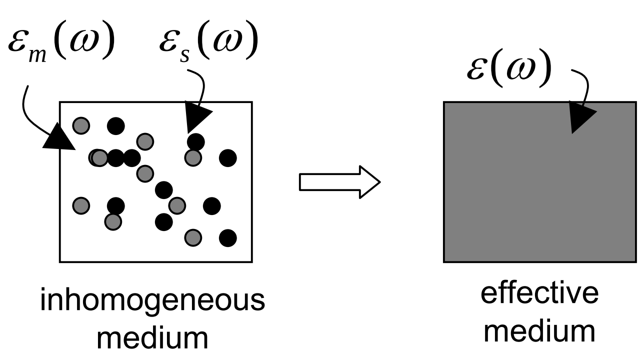
$$\varepsilon_m(\omega) = \varepsilon_\infty - \frac{\omega_p{}^2}{\omega^2 + i\gamma\omega}$$

Drude model for metal

$$\varepsilon_s(\omega) = \varepsilon_\infty - \frac{\omega_p{}^2}{\omega^2 - \omega_o{}^2 + i\Gamma\omega}$$

Lorentzian model for semiconductor

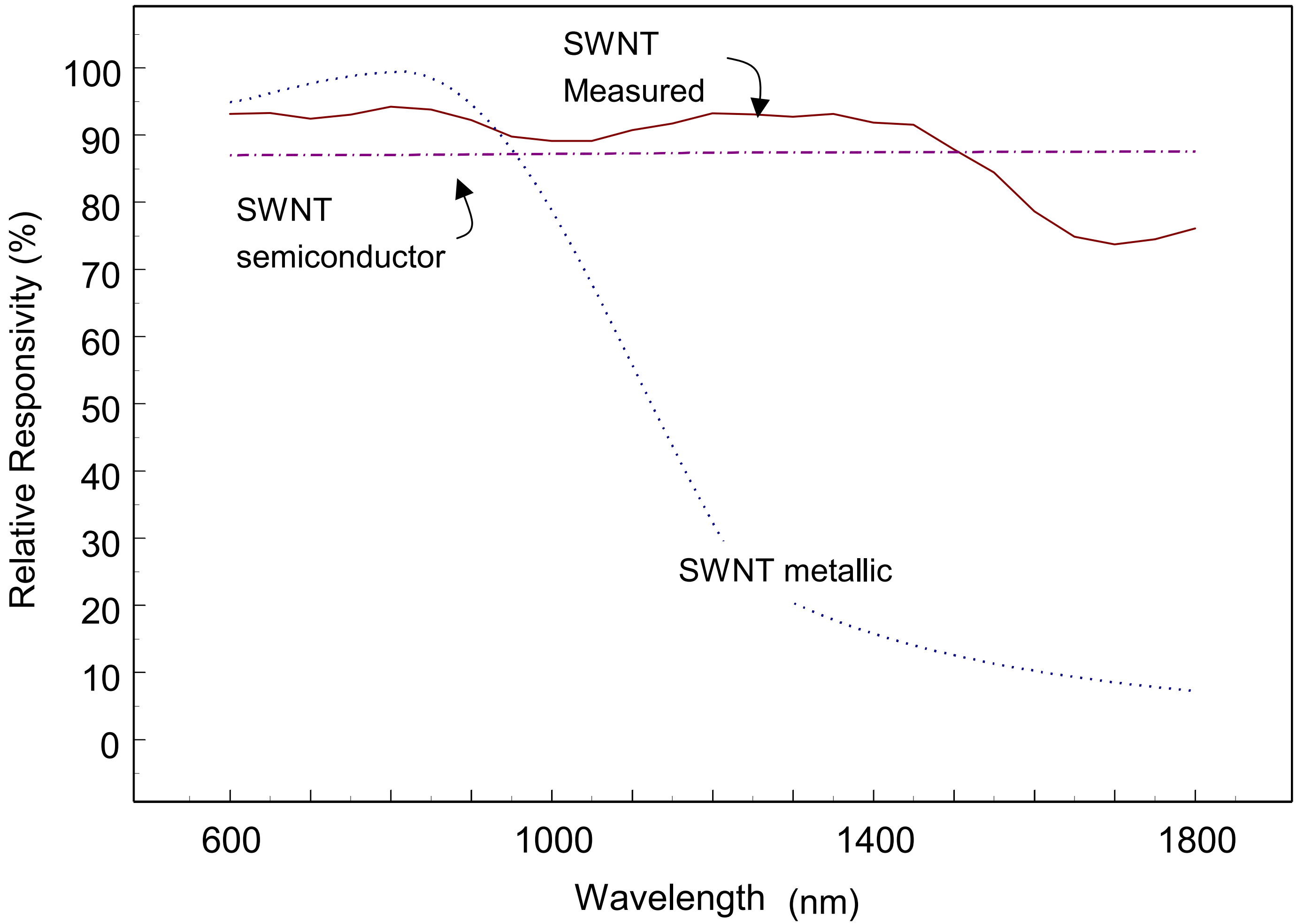
$$f\,\frac{\varepsilon_m - \varepsilon}{g\varepsilon_m + (1-g)\varepsilon} + (1-f)\,\frac{\varepsilon_s - \varepsilon}{g\varepsilon_s + (1-g)\varepsilon} = 0$$



$\varepsilon_m(\omega), \varepsilon_s(\omega)$	dielectric function
ε_∞	electronic core contribution
γ, Γ	relaxation rate of charge carriers
ω_p	plasma frequency of charge carriers
ω, ω_o	frequency, center frequency
f, g	fill factor, depolarization factor

A. Ugawa et al., Far-infrared gaps in single-wall carbon nanotubes, Phys. Rev. B, **60**, (1999).

Measured and expected detector response



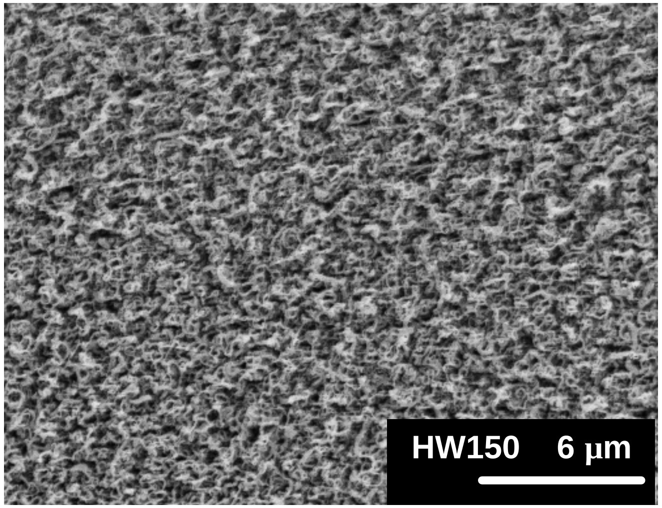
Questions:

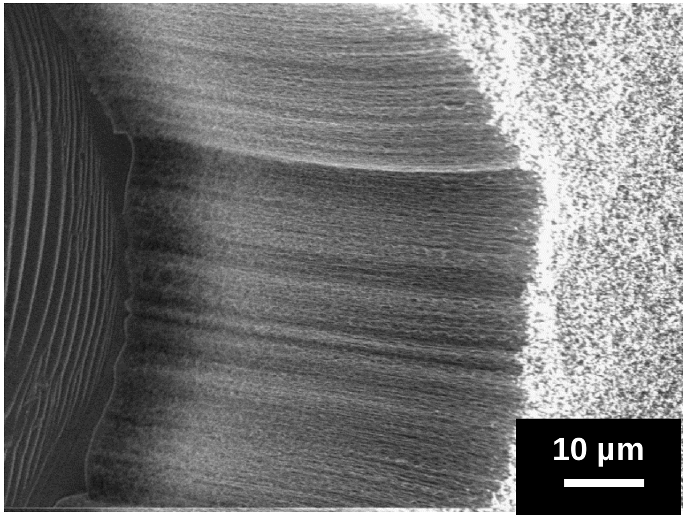
f ~ 10 %

morphology

Based on index calculated from composite dielectric function; 60 µm thick, $LiTaO_3$, with Ni electrodes

Aligned tubes on detectors

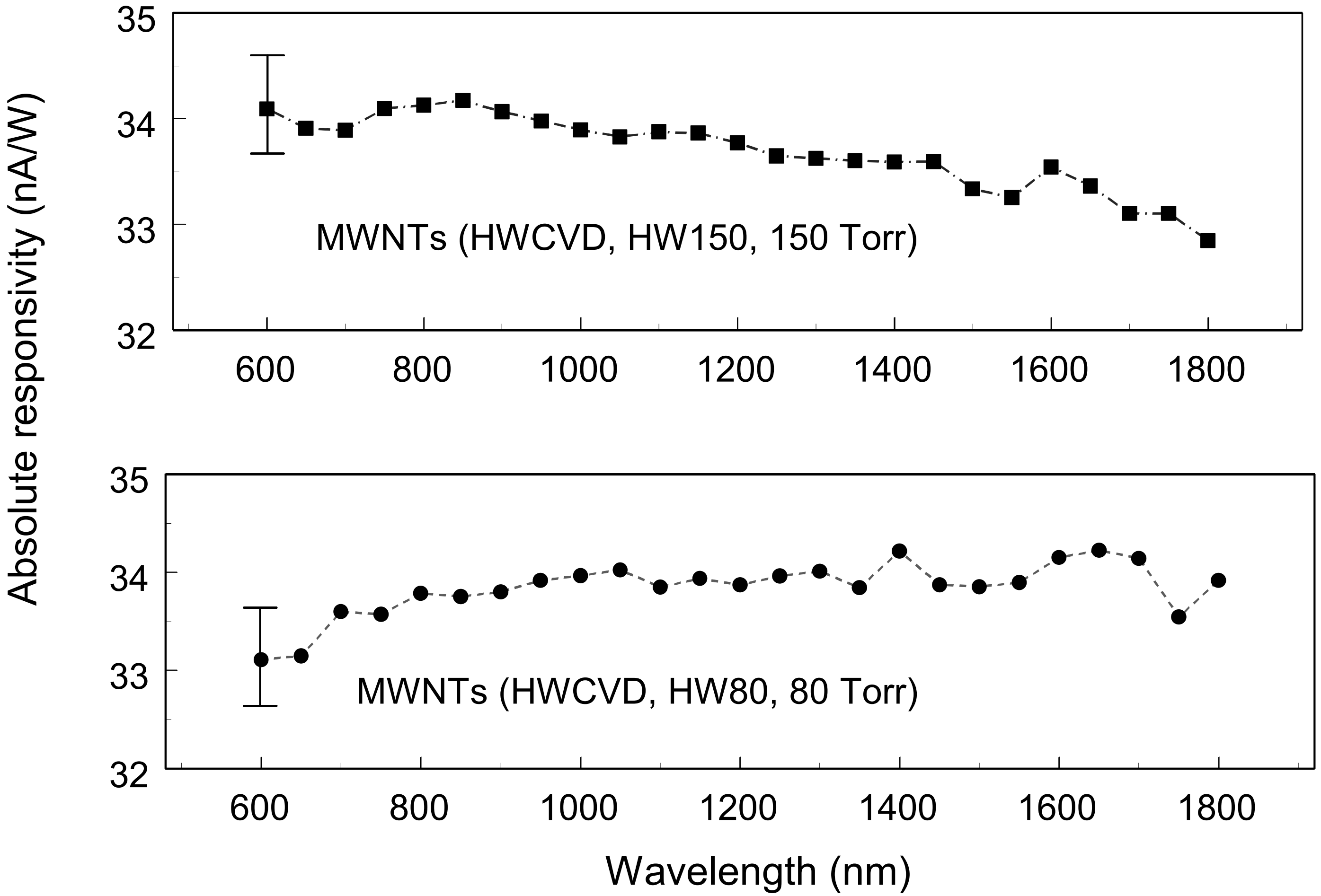




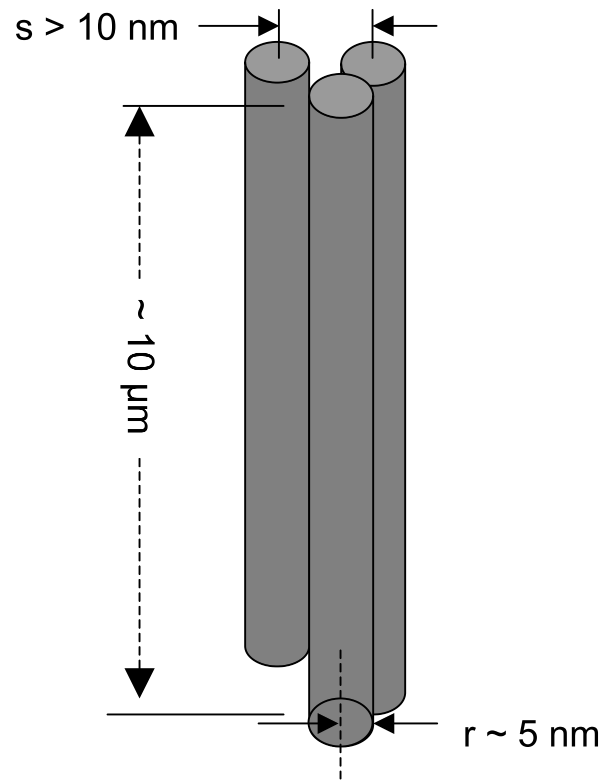
HWCVD on $LiNbO_3$

CVD on $LiNbO_3$

Measured detector response

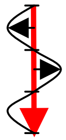


EMA for aligned cylinders

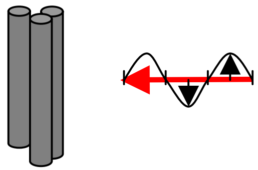


$$\boxed{\varepsilon^{p} = \frac{\varepsilon_{\|}(\omega)+\Delta+f\left(\varepsilon_{\|}(\omega)-\Delta\right)}{\varepsilon_{\|}(\omega)+\Delta-f\left(\varepsilon_{\|}(\omega)-\Delta\right)}}$$

$$f \approx \frac{\left(\pi r_{tube}^{2}\right)n_{tubes}}{Area_{detector}} \qquad \boxed{\Delta = \sqrt{\frac{\varepsilon_{\|}(\omega)}{\varepsilon_{\perp}(\omega)}}}$$



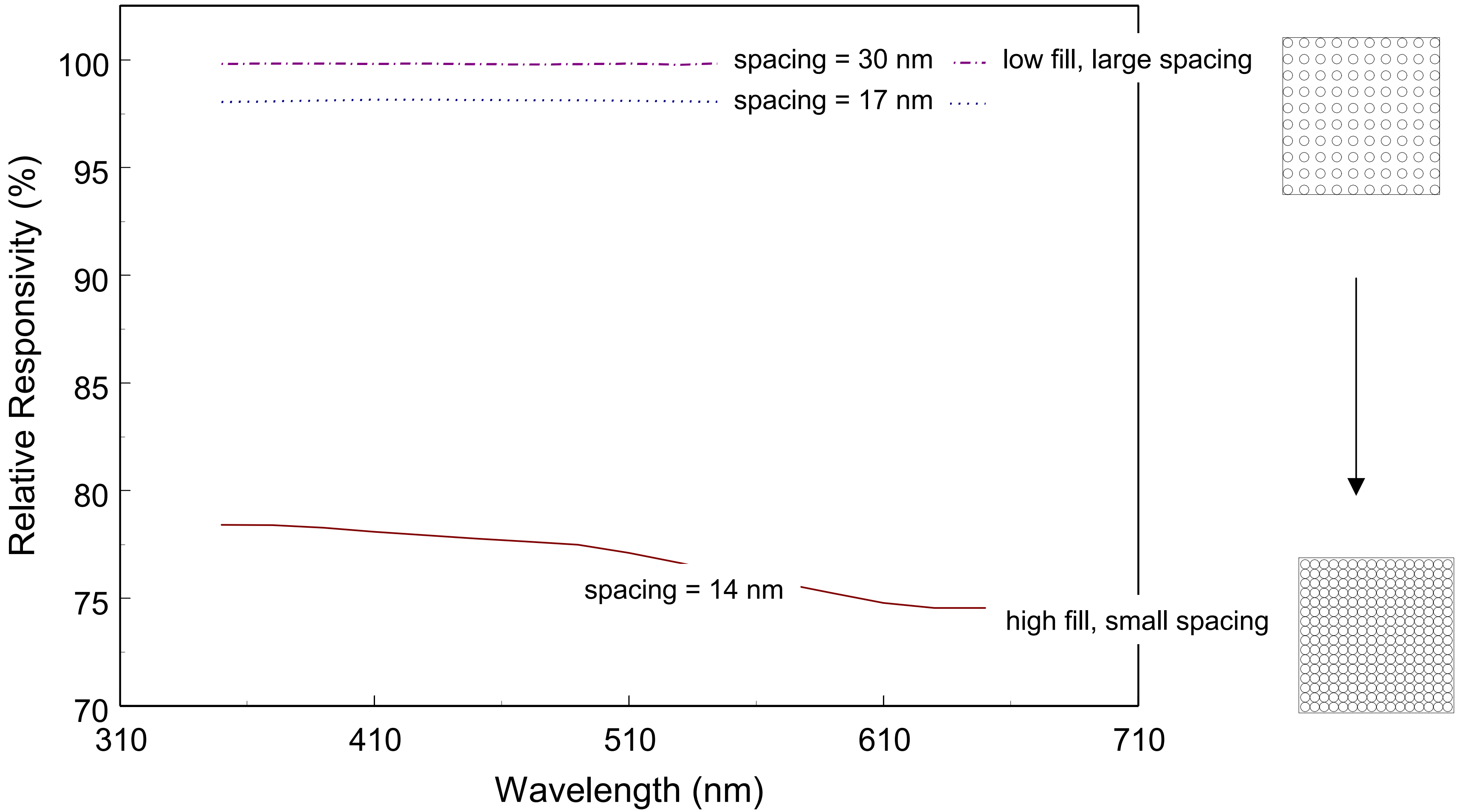
p polarization, ***E*** perpendicular to tube
(optical response depends on $\varepsilon_{\|}$ and $\varepsilon_{\perp}$ for graphite)



s polarization, ***E*** directed along tube
(optical response depends only on $\varepsilon_{\perp}$ for graphite)

* García-Vidal, et al., Phys. Rev. Lett., **78**, 4289-4292 (1997)

EMA, calculated results



Based on index calculated from composite dielectric function;
60 µm thick, $LiTaO_3$, with nickel electrodes

EMA and spectral responsivity measurements

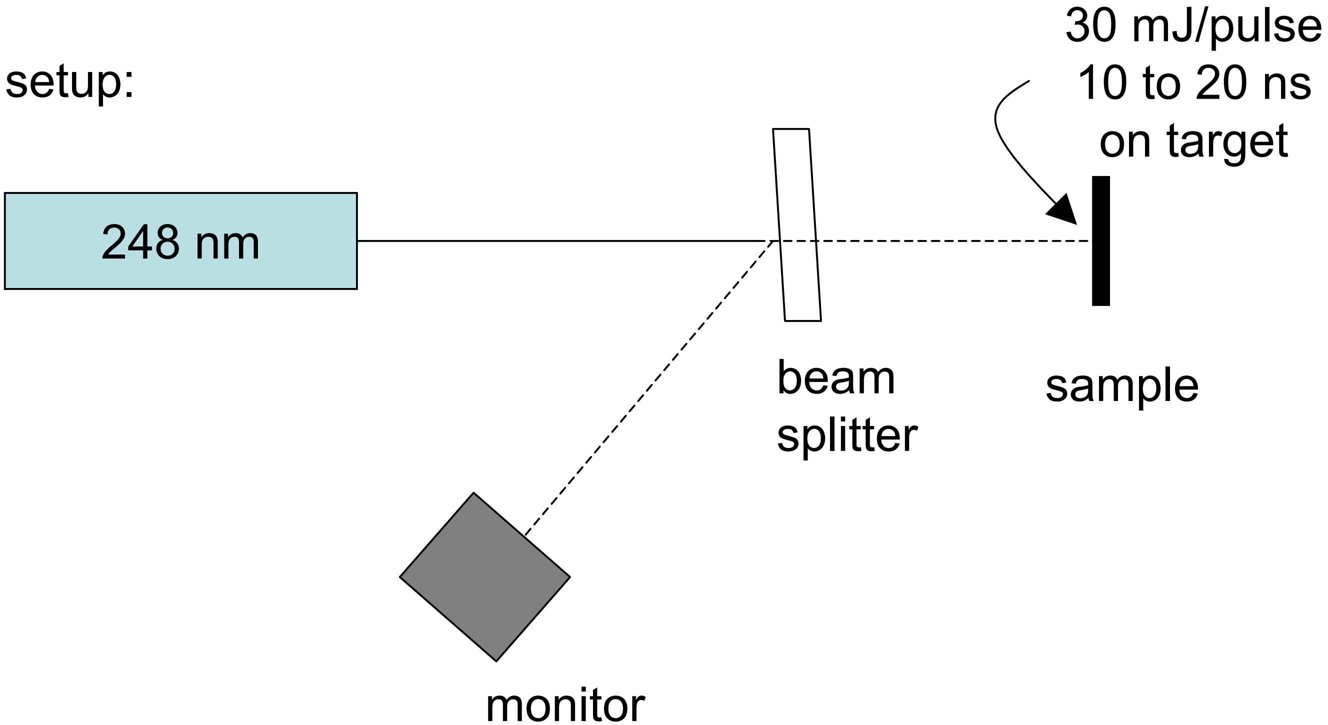
Implies a simple spectral responsivity measurement on bulk tubes can indicate metallic or semiconductor tubes present with ~ 10 % uncertainty.

(1) Is it valid for a mixture representing portions of SWNTs that are semiconductor and metallic?
(2) To what extent is the topology of the SWNT coating important; that is, the roughness, physical structure, proximity or entanglement of tubes with each other, compared to the crystal structure of the nanotubes?
(3) Finally, (a grand challenge) if there is a specific chirality of SWNT that is preferable, can it be isolated?

Cleaning to enhance responsivity

Investigation of laser-induced damage to SWNT-coated substrates

setup:



50 mJ/pulse visible ablation

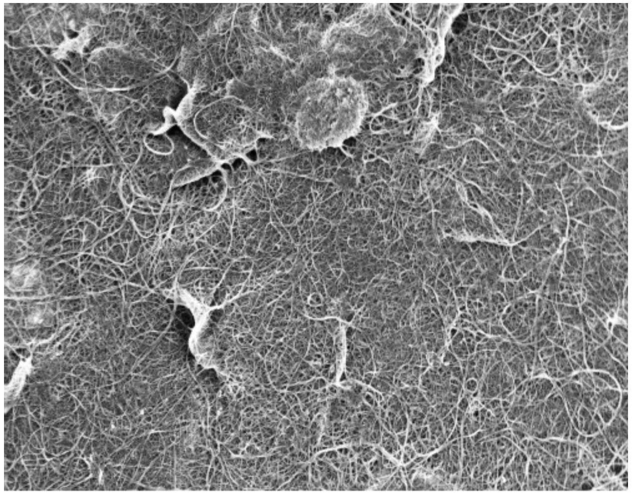
30 mJ/pulse visible change – thinner but blacker appearance

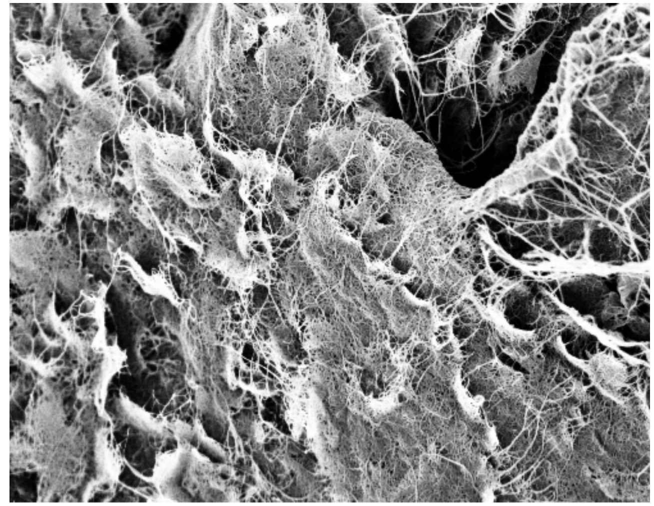
15 mJ/pulse no change

HRSEM qualitatively indicates lower density without altering tubes

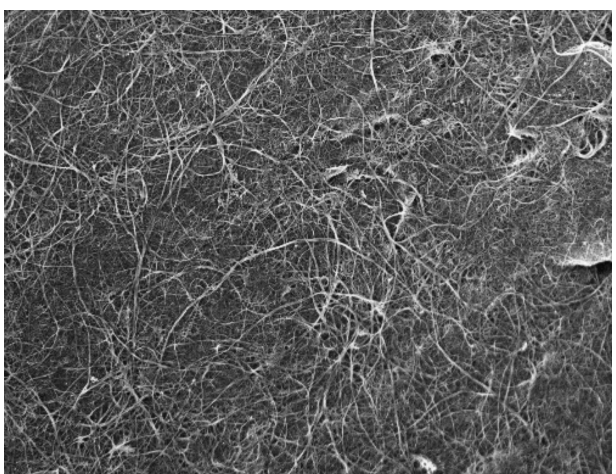
Cleaning

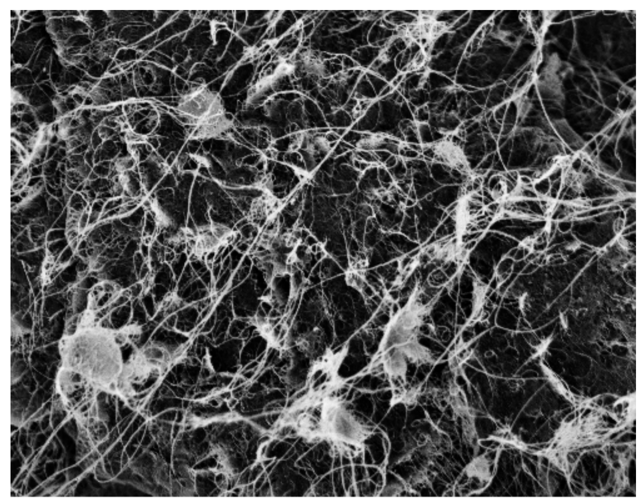
Before	After





SWNT bundles
on
silicon carbide

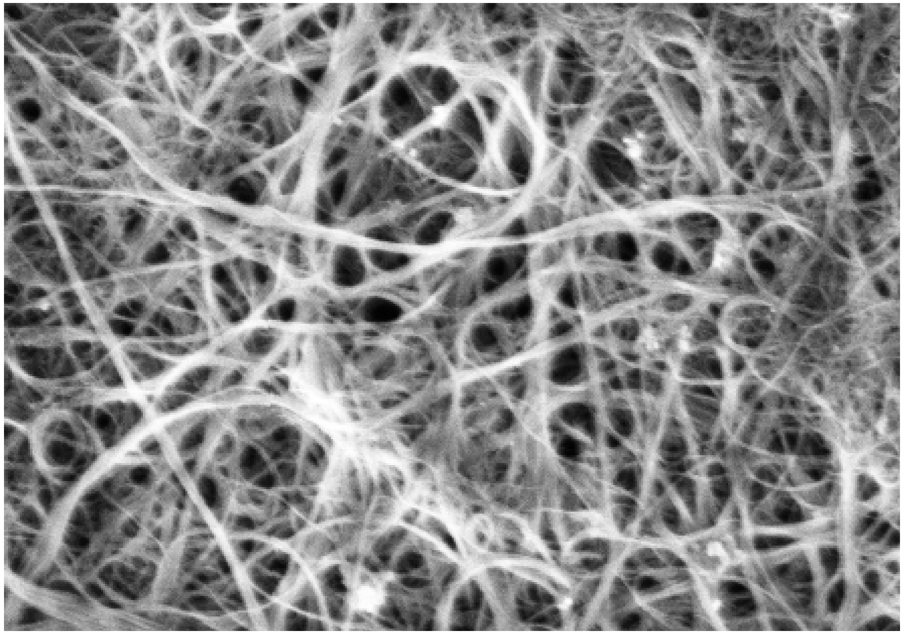




SWNT bundles
on
Cr:quartz

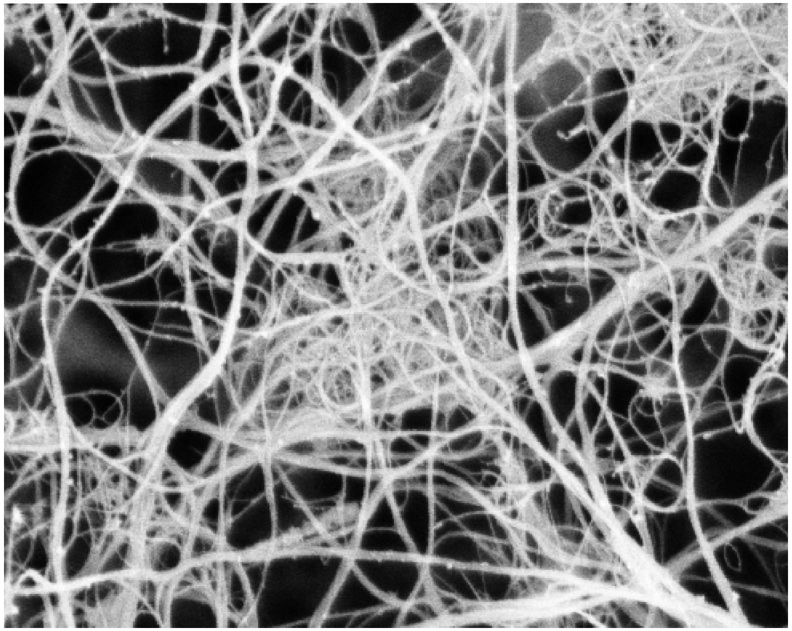
Also see: J.S. Kim, et al., Appl. Phys. Letts., **82**, (2003).

Cleaning



LiTaO3 thin sample

1µm 25000X



LiTaO3 after

1µm

SWNT bundles on $LiTaO_3$

Conclusion and acknowledgements

Detector development is immediate, practical, achievable

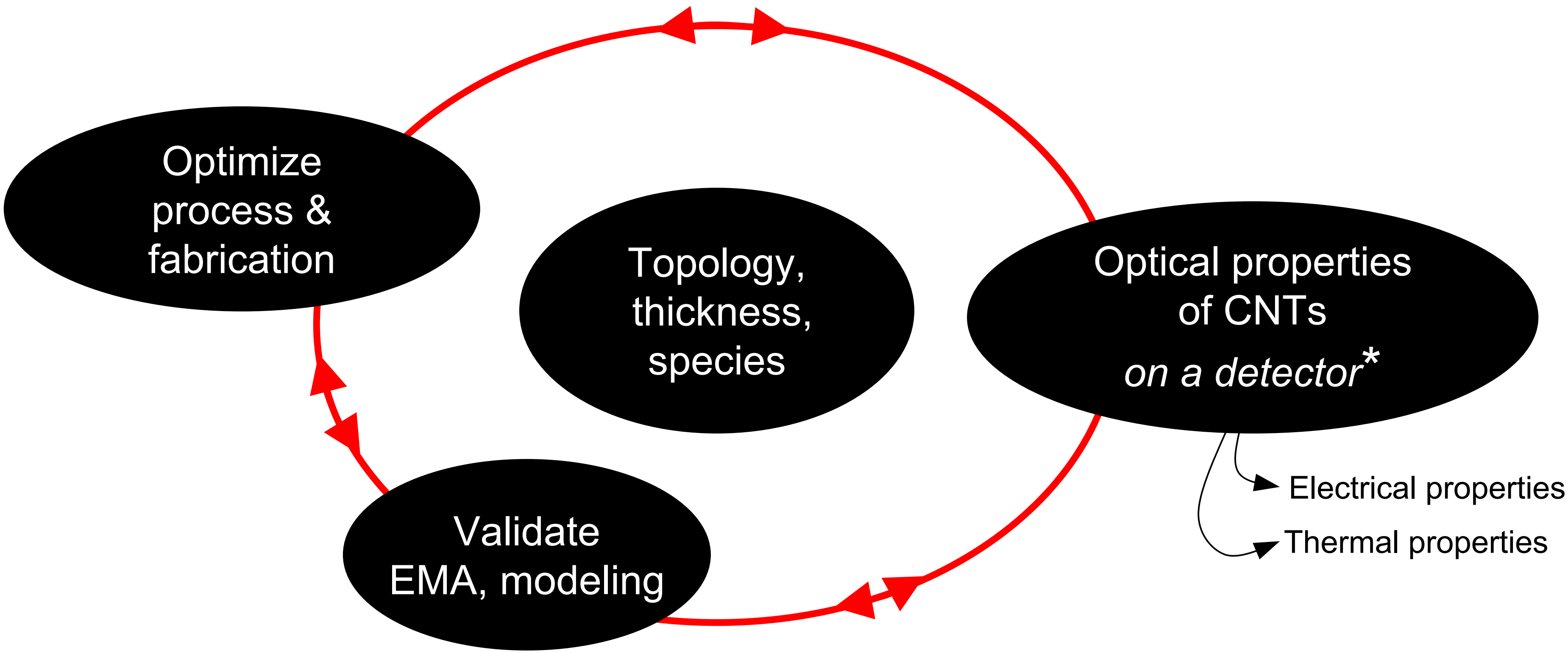
Science: unique situation of evaluating optical properties by
specular absorptance at normal incidence – relatively quickly

Future – CNTs on ferroelectrics or other detector platforms, EMA
need enriched samples and varied topology
of aligned tubes to verify the EMAs
Electrical properties, Thermal properties

Thanks to NIST, NREL, NPL

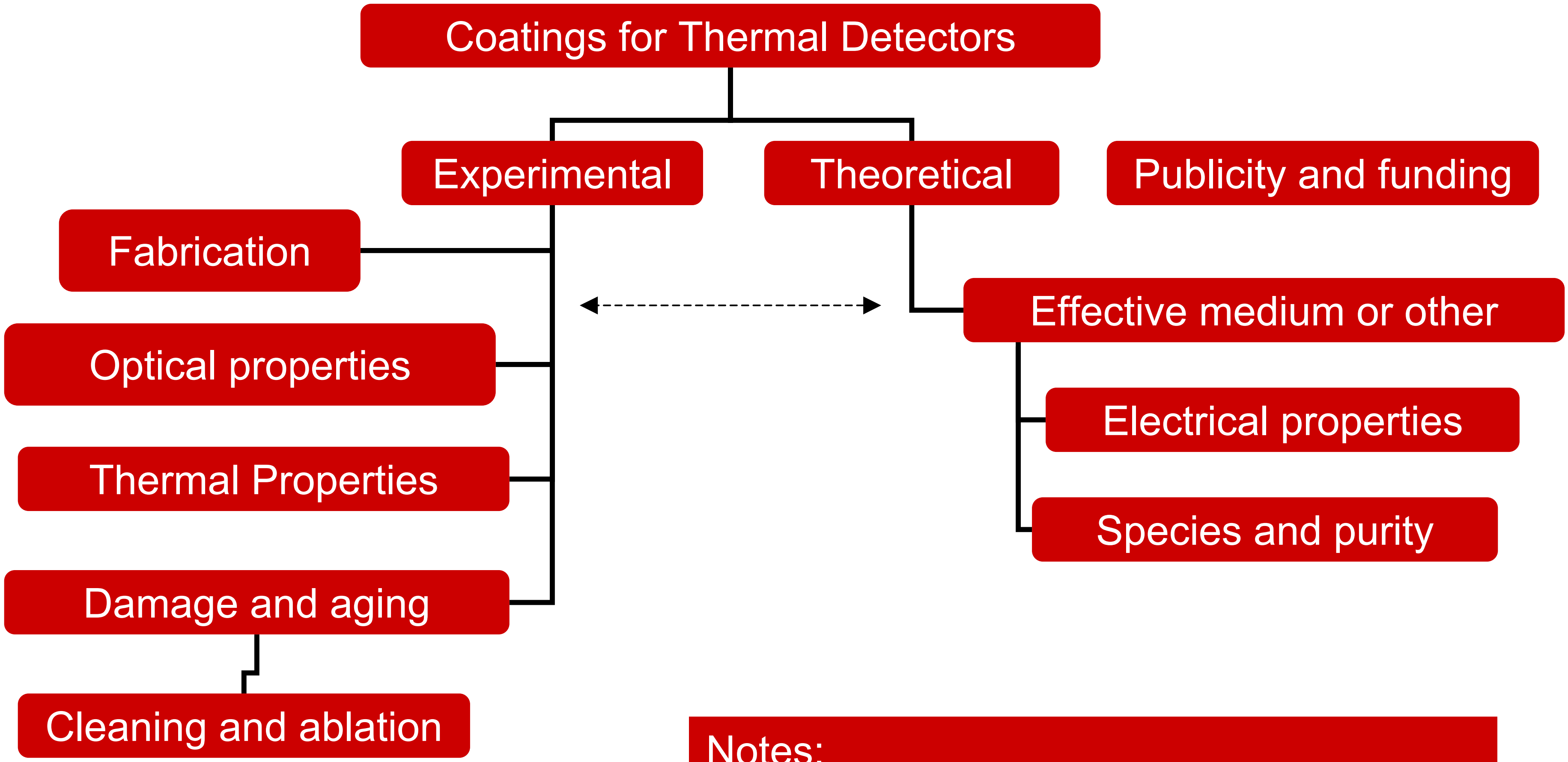
looking for an NRC post-doc

Challenges



* specular absorptance at normal incidence
vs.
small diffuse reflectance

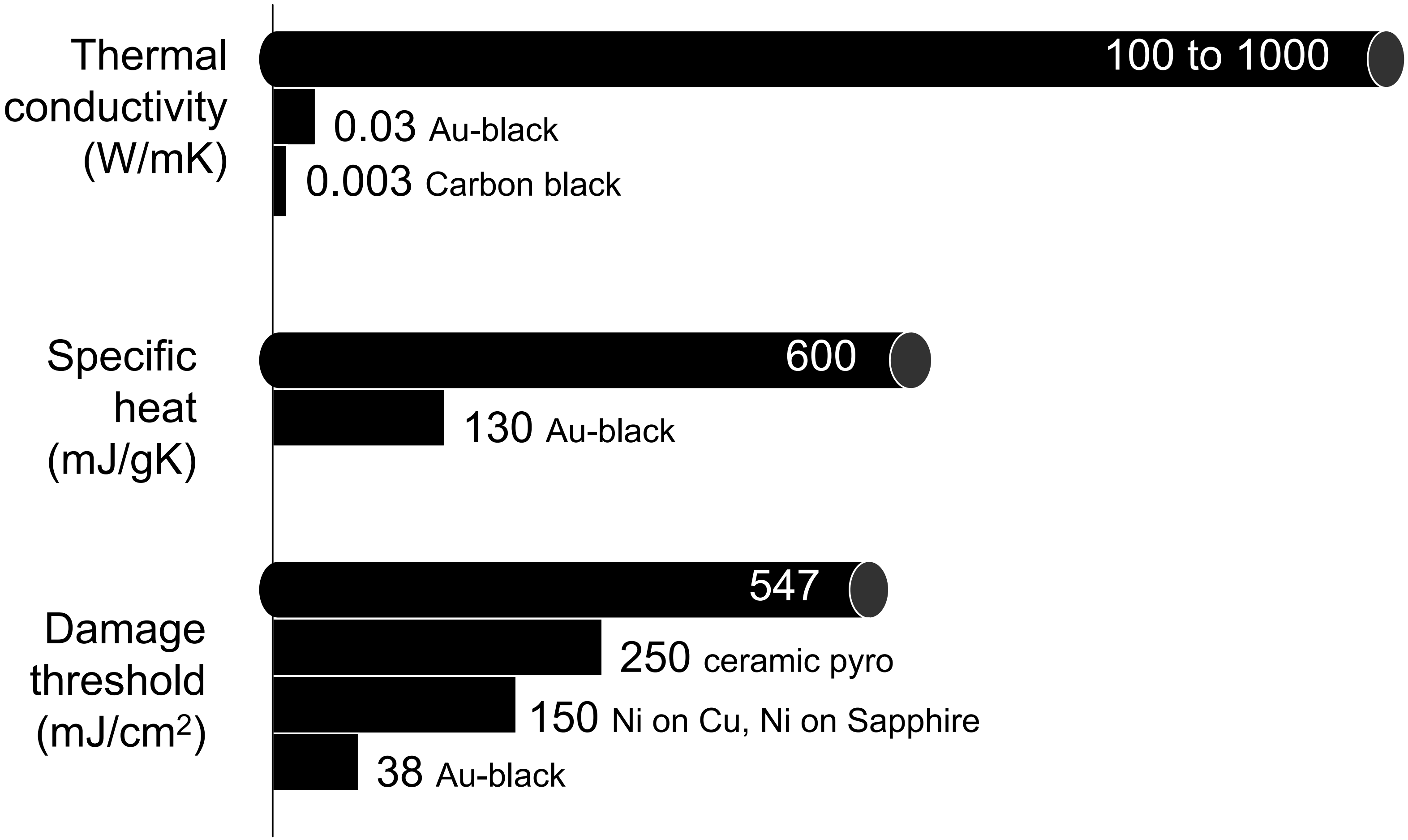
Challenges



Notes:

- index missing for vis, near uv for graphite
- iterate on SWNTs, MWNTs

Critical properties



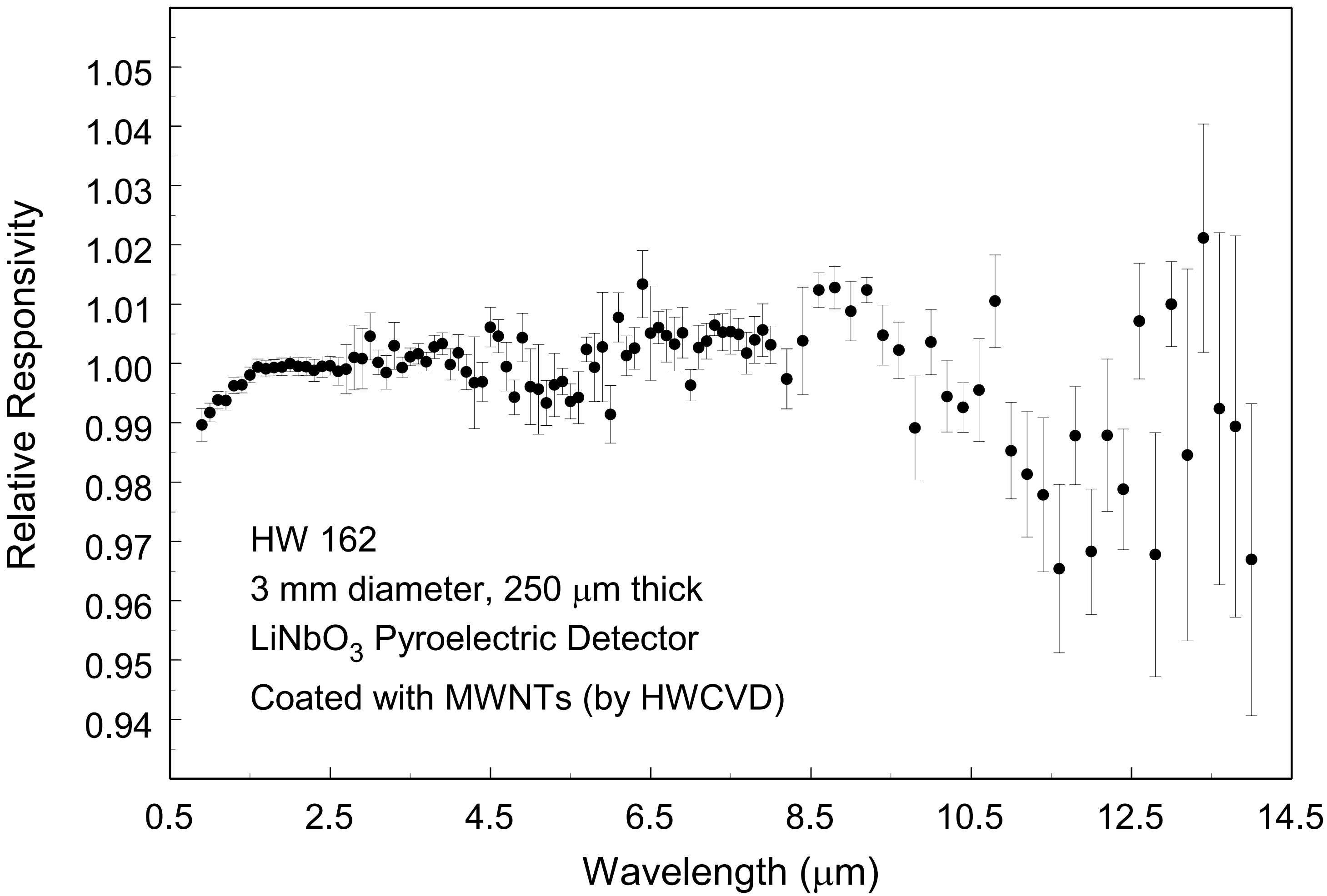
S.Berber, Y. Kwon, and D. Tománek, "Unusually High Thermal Conductivity of Carbon Nanotubes," Phys. Rev. Lett., **84**, (2000).

Blevin and Geist, Appl Opt. 13 1171 – 1178, 1974

Hone, Appl. Phys. A 74, 339–343 (2002)

J. S. Kim, K. S. Ahn, C. O. Kim, and J. P. Honga, "Ultraviolet laser treatment of multiwall carbon nanotubes grown at low temperature," Appl. Phys. Lett. **82**, (2003).

Measured detector response



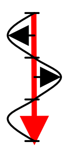
Modeling optical Properties (existing work)

missing data

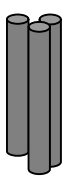
$$\varepsilon_{\perp} = n_o^2(1-k_o^2), \quad \varepsilon_{\parallel} = n_e^2(1-k_e^2)$$

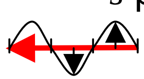
$$\hat{\varepsilon}(x,y,\omega) = \begin{pmatrix} \frac{x^2}{r^2}\varepsilon_{\parallel} + \frac{y^2}{r^2}\varepsilon_{\perp} & \frac{xy}{r^2}(\varepsilon_{\parallel}-\varepsilon_{\perp}) & 0 \\ \frac{xy}{r^2}(\varepsilon_{\parallel}-\varepsilon_{\perp}) & \frac{y^2}{r^2}\varepsilon_{\parallel} + \frac{x^2}{r^2}\varepsilon_{\perp} & 0 \\ 0 & 0 & \varepsilon_{\perp} \end{pmatrix}$$

Graphite is birefringent



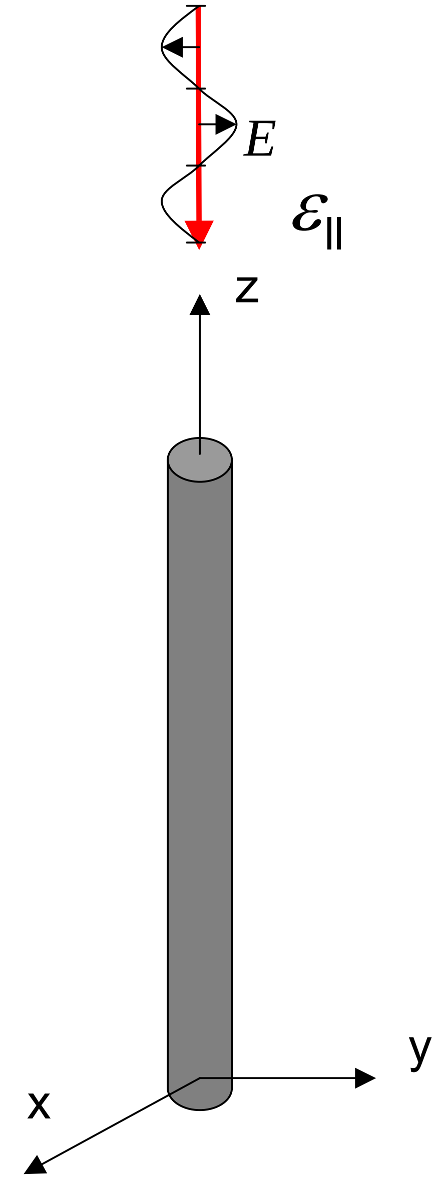
p polarization, $\boldsymbol{E}$ perpendicular to tube
(optical response depends on $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$)



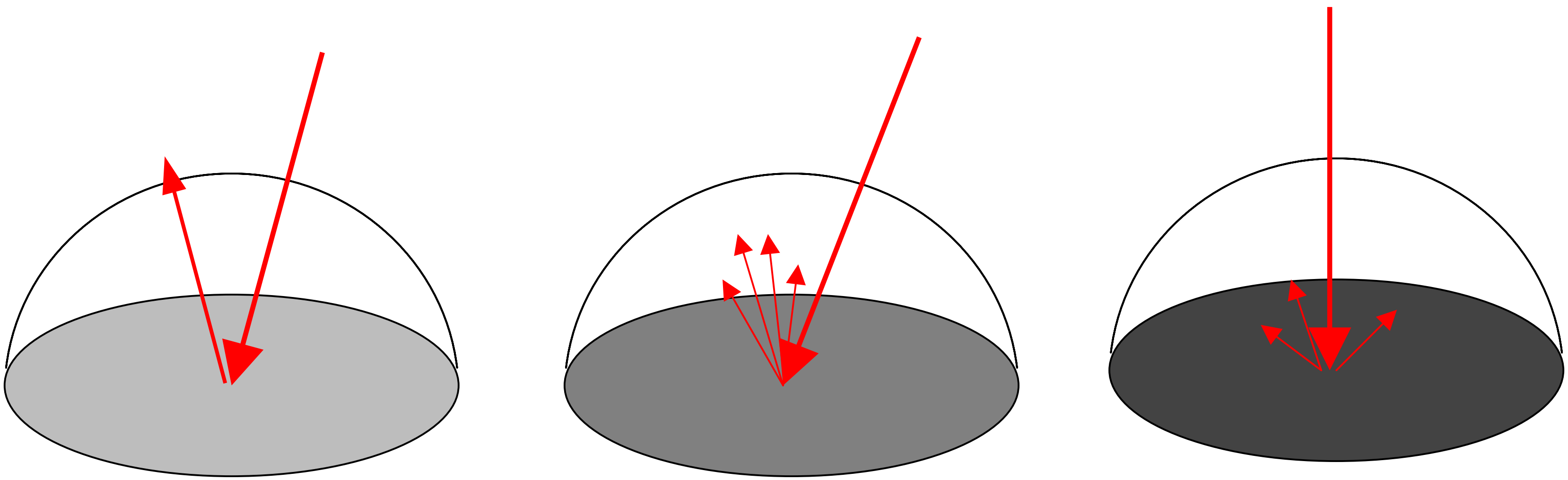


s polarization, $\boldsymbol{E}$ directed along tube
(optical response depends only on $\varepsilon_{\perp}$)

$$\varepsilon^s = f\,\varepsilon_{\perp}(\omega) + (1-f)$$



Optical properties

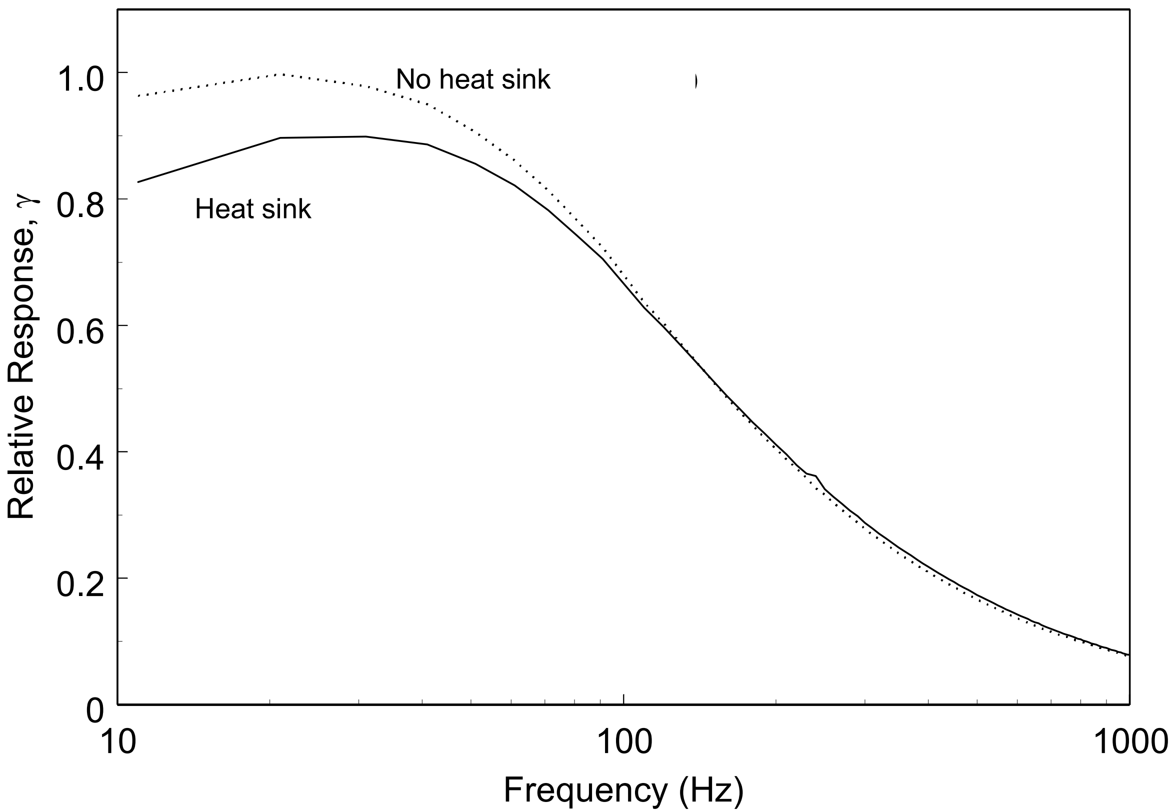


Specular absorptance
directional
specular reflectance

Specular absorptance
directional
diffuse reflectance

Specular absorptance
hemispherical
diffuse reflectance

Freestanding pyroelectric detectors are preferred



+ sensitivity
+ spatial uniformity
+ thinner is better

- acoustic sensitivity

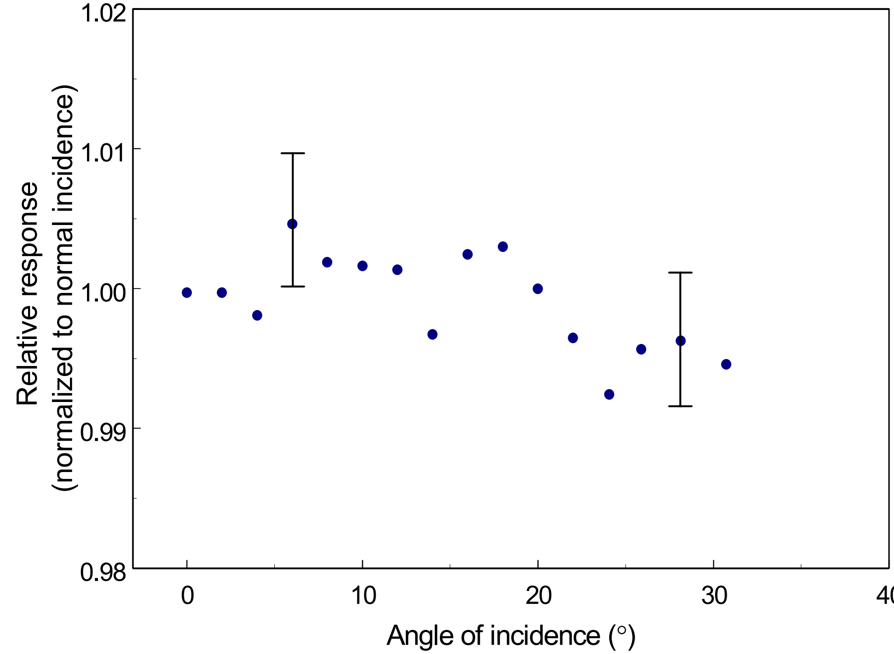
$$i = p\frac{A}{h}\int_0^h \frac{d\theta}{dt}dz$$

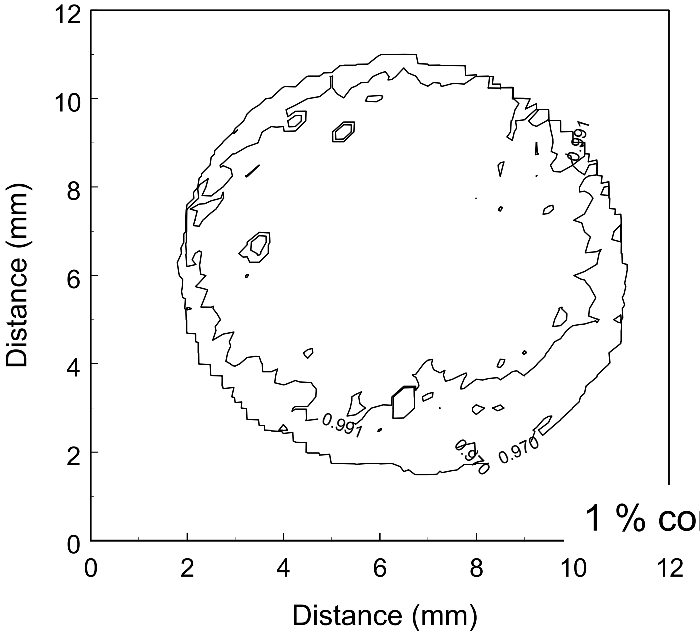
Holeman, Phelan, Peterson

(1) Is it valid for a mixture representing portions of SWNTs that are semiconductor and metallic?
(2) To what extent is the topology of the SWNT coating important; that is, the roughness, physical structure, proximity or entanglement of tubes with each other, compared to the crystal structure of the nanotubes?
(3) Finally, (a grand challenge) if there is a specific chirality of SWNT that is preferable, can it be isolated?

$$\hat{\varepsilon}(\omega) = \varepsilon_{\perp}(\omega)(\theta\theta + \mathrm{zz}) + \varepsilon_{\parallel}(\omega)\,\mathrm{rr}$$

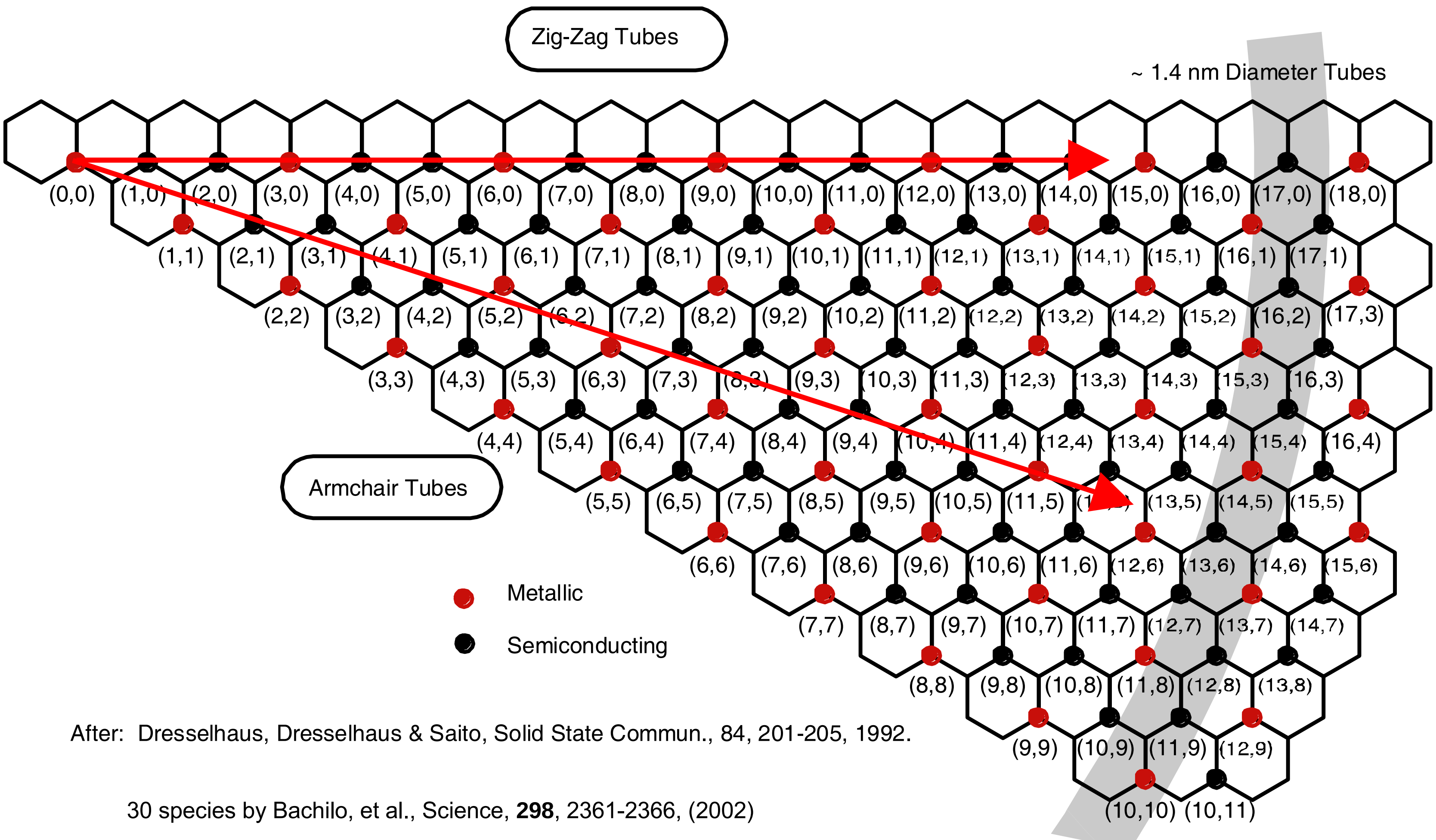
Spatial and directional uniformity





1 % contour interval

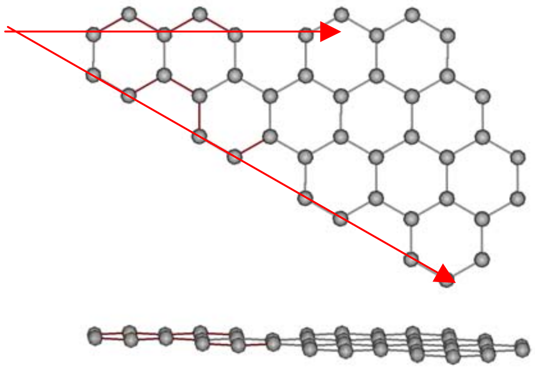
0.25 mm increments
0.5 mm beam, 850 nm



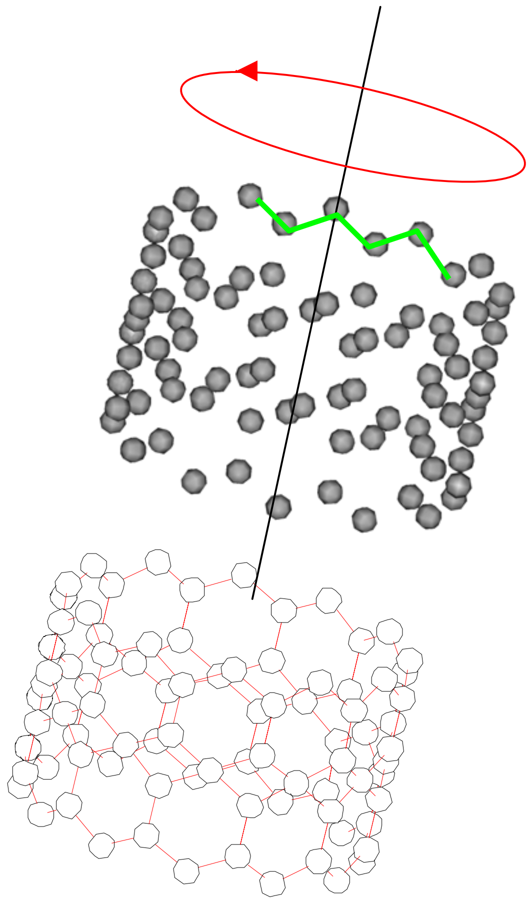
After: Dresselhaus, Dresselhaus & Saito, Solid State Commun., 84, 201-205, 1992.

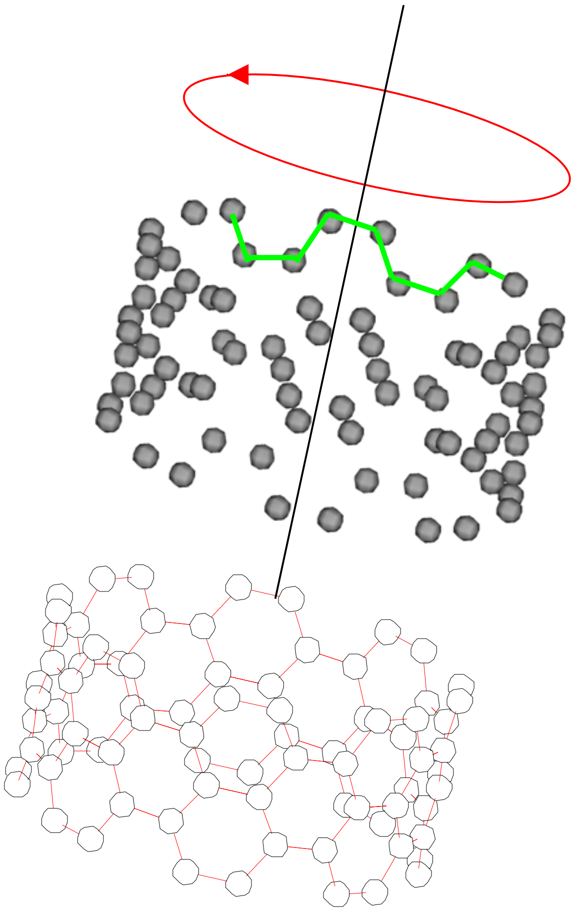
30 species by Bachilo, et al., Science, **298**, 2361-2366, (2002)

Carbon nanotubes



graphene





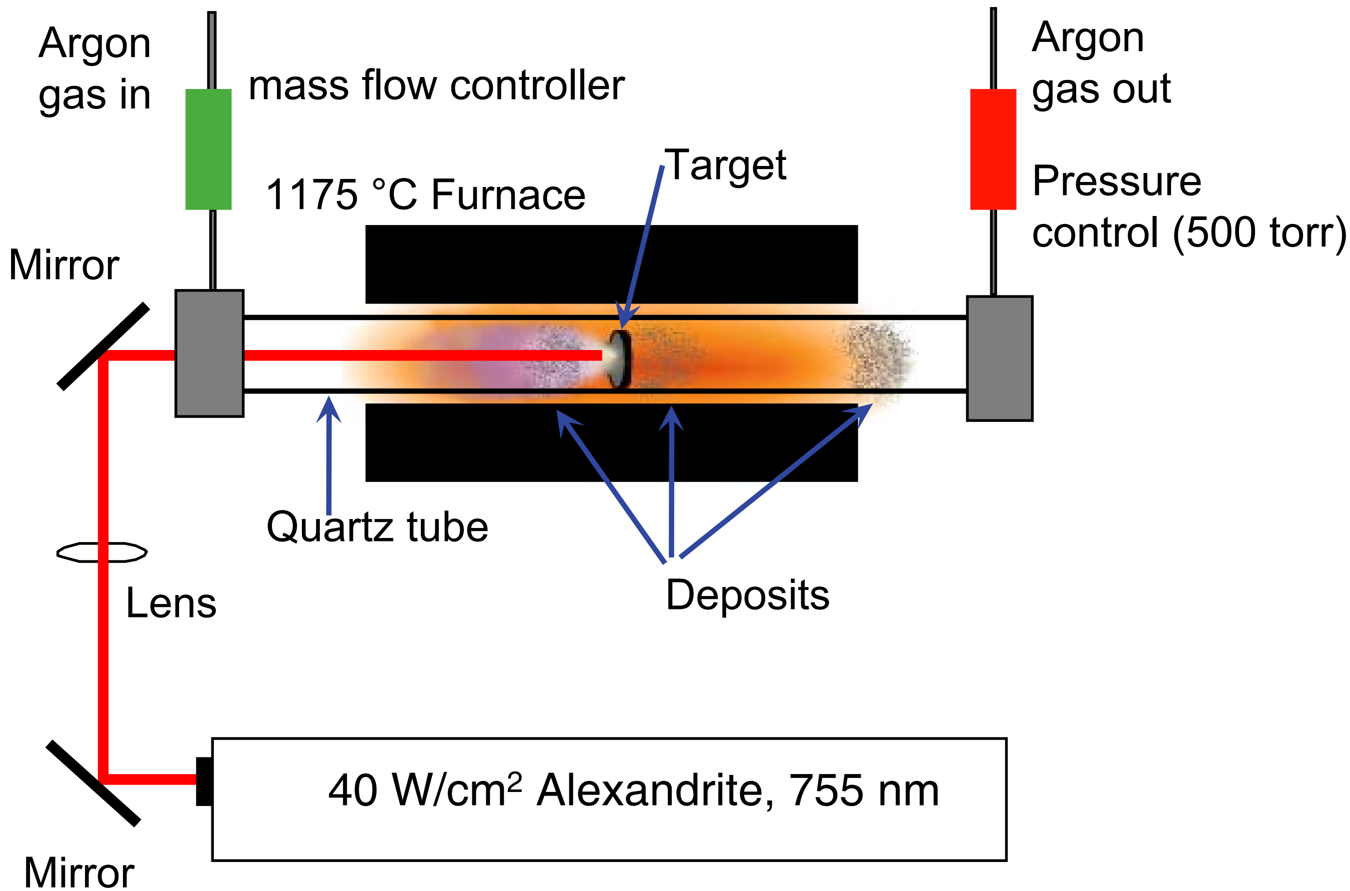
zigzag
(metal or semiconductor)

armchair (metal)

Dresselhaus, Dresselhaus, Saito, Solid State Comm., 84, 201-205, 1992

30 species by Bachilo, et al., Science, **298**, 2361-2366, (2002)

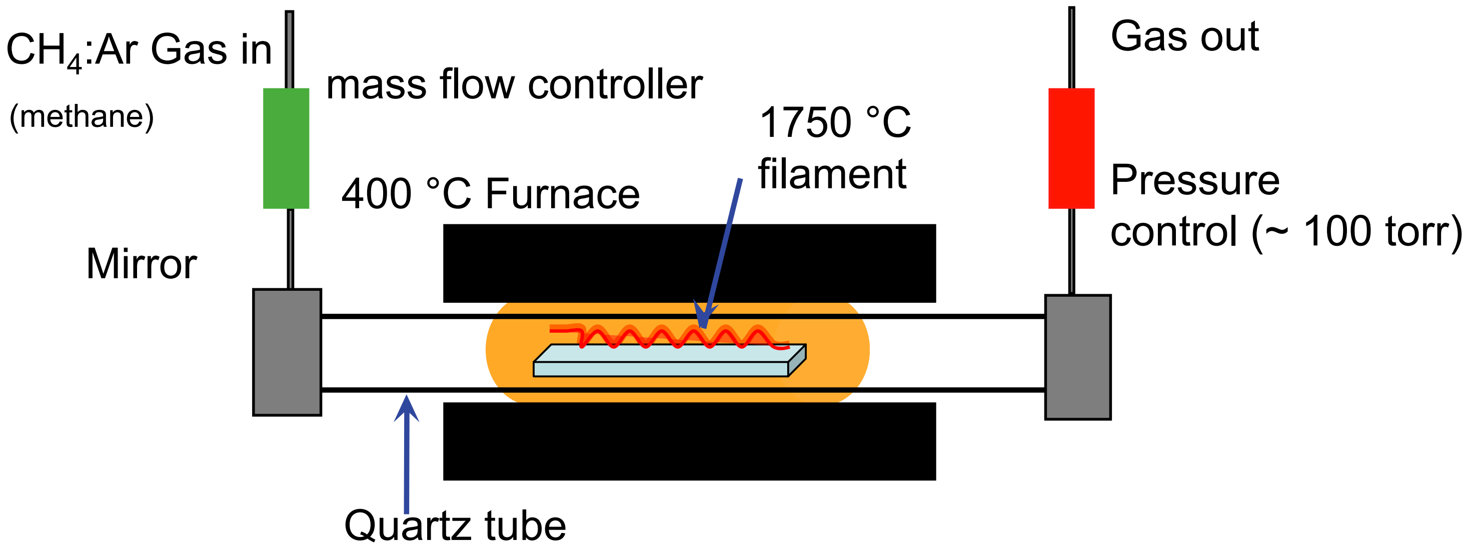
Laser synthesis of carbon single-wall nanotubes (SWNTs)



T. Guo, P. Nikolaev, A. Thess, D. T. Colbert, and R. E. Smalley, "Catalytic growth of Single-walled Nanotubes by Laser Vaporization" Chemical Physics Letters **243,** 49-54 (1995).

C. Dillon, T. Gennett, K. M. Jones, J. L. Alleman, P. A. Parilla, M. J. Heben, A simple and complete purification of single-walled carbon nanotube materials. Adv. Mater. **11**, 1354-1358 (1999).

Hot wire chemical vapor deposition (HWCVD) synthesis of aligned MWNTs



A.H. Mahan, J.L. Alleman, M.J. Heben, P.A. Parilla, K.M. Jones and A.C. Dillon, Appl. Phys. Lett. 81 (2002) 4061.